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J. Leifeld, U. Franko, E. Schulz. Thermal stability of soil organic matter responds to long-term fertilization practices. *Biogeosciences Discussions*, 2006, 3 (2), pp.309-320. hal-00297793

HAL Id: hal-00297793

<https://hal.science/hal-00297793>

Submitted on 4 Apr 2006

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Thermal stability of soil organic matter responds to long-term fertilization practices

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Received: 18 January 2006 – Accepted: 7 February 2006 – Published: 4 April 2006

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Abstract

We used differential scanning calorimetry (DSC) to infer thermal properties of soil organic matter (SOM) in the static fertilization experiment in Bad Lauchstädt, Germany, which has been established in 1902. Four treatments (null N, change from null to manuring in 1978 NM, change from manuring to null in 1978 MN, and permanent manure and mineral fertilization since 1902 M) were sampled in 2004. Soil organic carbon contents were highest for M (2.4%), lowest for N (1.7%), and similar for MN and NM (2.2%). DSC thermograms were characterized by three peaks at around 354, 430, and 520°C, which were assigned to as thermally labile and stable SOM and combustion residues from lignite, respectively. DSC peak temperatures were relatively constant among treatments, but peak heights normalized to the organic C content of the soil were significantly different for labile and stable SOM. Labile C was higher for M>MN=NM=N, and stable C decreased in the order N=NM>MN=M, showing that agricultural depletion of SOM increases the share of thermally stable C. Lignite-derived C was not affected by management, suggesting a homogeneous deposition across treatments.

1 Introduction

Measurement of the thermal behaviour of organic matter under oxidative conditions allows separating thermally labile and stable compounds by means of measuring peak temperatures, for example. It has been suggested, that the thermal stability of plant tissue is closely related to its chemistry (Shafizadeh, 1984), but the conceptual linkage between chemical and physical properties of organic matter in soil and its thermal reactivity is less straightforward. For sites under contrasting agricultural land-use, Lopez-Capel et al. (2005) showed that free and intra-aggregate light fractions of soil organic matter (SOM) are characterized by typical thermal responses and that thermal and chemical attributes of the organic matter were correlated. Also clay fractions in chronosequences from native forest to long-term bare fallow differed in their thermal

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stability and the bare fallow was relatively enriched in stable organic matter (Plante et al., 2005). Thermal properties of bulk soils from long-term arable treatments under different fertilization regime have to our knowledge not been investigated so far and are subject of this paper.

5 Differential scanning calorimetry measures the differential heat flow of a sample (endo- or exotherm) relative to a reference as a function of temperature. Because thermal data are obtained relative rapidly and their measurement requires little sample preparation, thermal stability may have the potential to serve as an indicator for more complex attributes which are otherwise difficult to obtain, such as the distribution of
10 SOM between biochemical labile and stabile fractions (Grisi et al., 1998). Moreover, measurements of coals and soot indicate that these compounds have thermal properties very much distinct from that of relatively recent, biogenic organic matter (hereafter called “natural”) (Garcia et al., 1999; Boehman et al., 2005). Thus, a thermal screening might also help to distinguish between natural and coal or thermally altered organic
15 matter.

2 Material and methods

Samples were taken in 2004 at different days of the year ($n=7$) from four treatments of the Extended Static Fertilization Experiment in Bad Lauchstädt, close to the city of Halle, Germany ($51^{\circ}24' \text{ N}$, $11^{\circ}53' \text{ E}$, altitude 113 m above sea, mean annual precipitation 484 mm, mean annual temperature 8.7°C). The soil is a loamy Haplic Chernozem
20 (FAO) with 22% clay. Total field size is 3.09 ha with individual parcels covering 265 m^2 . This long term experiment consists of plots with continuous treatment since 1902 and a set of treatments that has been altered in 1978. The latter include organic matter-depleted plots that now receive farmyard manure and plots with former high SOM levels
25 where farmyard manure application is now terminated. Four treatments (null N, change from null to manuring in 1978 NM, change from manuring to null in 1978 MN, and permanent manure and mineral fertilization since 1902 M) were sampled from 0 to 20 cm.

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In the M plots, 30 t ha⁻¹ farmyard manure is applied every second year (crop rotation: sugar beet, summer barley, potatoes, winter wheat). Detailed field set-ups are given in Körschens and Pfefferkorn (1998).

Thermograms were scanned with a differential scanning calorimeter DSC100 (TA Instruments) after heat flow calibration with Sapphire and temperature and heat calibration with the melting of Indium (Danley, 2003). In a range of previous experiments, we tested the dependence of the DSC parameters (heat flow, onset- and peak temperatures, and heat of reaction) on different sample C concentrations and derived an optimum sample weight of 0.2 to 0.5 mg C. For the results reported here, about 15 mg finely ground dry material was weighted into an open Aluminium pan. An empty Al-pan served as the reference. Samples were heated under a flow of synthetic air of 50 ml min⁻¹ from room temperature to 600°C at a heating rate of 20°C min⁻¹. This flow allowed oxidizing conditions at any one point of reaction. DSC parameters used to characterize the stability of the materials were peak temperatures (°C), peak heights (W g⁻¹ soil or normalised to the organic C content of the sample by dividing the thermogram through the organic C content, W g⁻¹ organic C), and total heat evolved (J g⁻¹). Peak heights were measured as the maximum deviation from a linear baseline drawn between 150 and 568°C.

Aliquots of the samples were HCl treated to remove carbonates, and organic carbon (OC) was measured after dry combustion in an O₂-stream and detection of the produced CO₂ by IR absorption.

Thermal parameters passed tests for normality and homogeneity of variances. An ANOVA followed by a Scheffé-test was used to identify treatment-induced differences of means, and Pearson's coefficient was calculated to check for correlation.

3 Results and discussion

Soil organic carbon contents were highest for M (2.38±0.03%; mean ± standard error), lowest for N (1.73±0.02%), and similar for MN and NM (2.16±0.02 and 2.18±0.05%,

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respectively). Historical records for all crops showed marked yield differences between N and M treatments. Together with the manure input this explains the differences in soil OC content (Körschens and Pfefferkorn, 1998). The total heat evolved during oxidation was highly significantly correlated with the OC content of the sample ($r=0.91$, $P<0.01$). We thus suggest that the exothermic reactions mostly derive from organic matter oxidation, and that the heat evolved is roughly proportional to the amount of organic matter in the sample.

Thermograms of all samples were virtually similar and characterized by three strong exotherms at around 354, 430, and 520°C, and one endotherm at around 576°C attributable to a phase transition of Quartz (Fig. 1). Peak temperatures of single exotherms were similar among the four treatments N, NM, MN, and M (first peak 354.5 ± 0.5 , 355.4 ± 0.7 , 354.3 ± 0.3 , 354.1 ± 0.3 , second peak 428.6 ± 0.8 , 430.8 ± 2.2 , 428.9 ± 1.1 , 429.5 ± 1.2 , third peak 520.6 ± 1.0 , 520.0 ± 0.9 , 522.0 ± 0.9 , 521.4 ± 1.5). Peak heights were more variable than peak temperatures and compared between i) the four treatments and ii) the seven different days of the year when samples were taken. The latter comparison revealed no systematic pattern because both, OC contents and thermal properties were related to the long-term fertilization regime rather than to variations throughout the year, and so only comparisons between treatments are reported.

Significant effects were found for peak heights of the first and second exotherm (Figs. 2 and 3). Because peak heights were normalized to the C content of each sample, the difference is attributable to a fertilization-induced variation in SOM quality. In terms of thermal stability, the Null plot was characterized by the smallest proportion of labile and the highest of stabilized OC, and this pattern was reversed for treatment M receiving mineral plus manure fertilizer since 1902. Though their OC content was the same, treatment effects between MN and NM could be clearly distinguished by peak heights of the second peak and by the ratio peak height peak one/peak height peak two (Fig. 4), implying a higher sensitivity of thermal properties than of the OC content to fertilization. Higher thermal stabilities of N compared to M treatments correspond to relatively higher proportions of labile OC in M than in N plots as measured by hot water

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extraction at the Bad Lauchstädt experiment (Körschens et al., 1998).

A direct comparison of peak temperatures between different DSC set-ups is hampered because peak temperatures are logarithmically related to the heating rate (ASTM, 2005). In a range of previous experiments we found that the Bad Lauchstädt exotherms at 520°C tracked at 20°C min⁻¹ correspond to peak temperatures of 496°C and 508°C at heating rates of 5 and 10°C min⁻¹, respectively, making data among different studies comparable to each other. The third peak is not typical for the oxidation of natural organic matter (see e.g. Dell'Abate et al., 2003; Shafizadeh, 1984), but exotherms above 500°C have been observed for the combustion of coals and soot (Sonibare et al., 2005; Garcia et al., 1999; Boehman et al., 2005). However, peak temperatures during the combustion of various lignites were typically below 500°C at a heating rate of 10°C min⁻¹ (Kök, 2001). It has been hypothesized before that some soils near the city of Halle are affected by deposition of lignite dust or lignite-derived combustion products due to their vicinity to open cast mining, railway lines and lignite power plants by means of chemical methods (Schmidt et al., 1996) and ¹⁴C dating (Rethemeyer et al., 2005). We suggest that lignite-derived reaction products rather than native lignite contribute to the thermal decomposable compounds at our site because the third peak occurred at higher temperatures than those in the study of Kök (2001).

Peak heights (0.316±0.013 W g⁻¹ soil) of the third peak were statistically not different between treatments. Therefore, it seems likely that the deposition was homogeneous over the whole experimental field and that possible alteration in the soil's biological activity induced by variations in residue returns and manure inputs did not induce preferences in the degradation of thermal stable material.

In conclusion, the DSC measurements of the Static Fertilization Experiment in Bad Lauchstädt clearly indicated qualitative differences of the SOM with higher thermal stabilities of long-term depleted plots. DSC parameters were found to be more sensitive to management than bulk soil C contents and may thus serve as indicators also for biochemical SOM attributes. The higher stability of lignite-derived products at this site

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refers to possible applications of DSC beyond the characterization of natural SOM.

Acknowledgements. The authors thank F. Müller for help in the lab.

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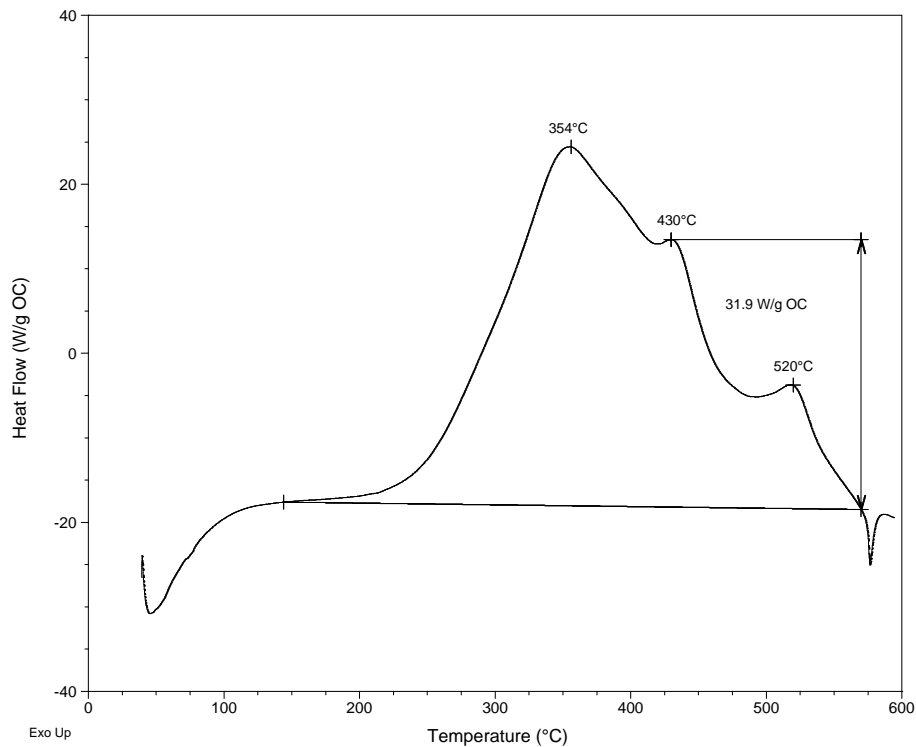


Fig. 1. DSC thermogram with exothermic peaks at 354, 430, and 520°C and the endothermic Quartz transition at 576°C. The distance between peak maximum and baseline for the peak at 430°C exemplifies how peak heights were measured.

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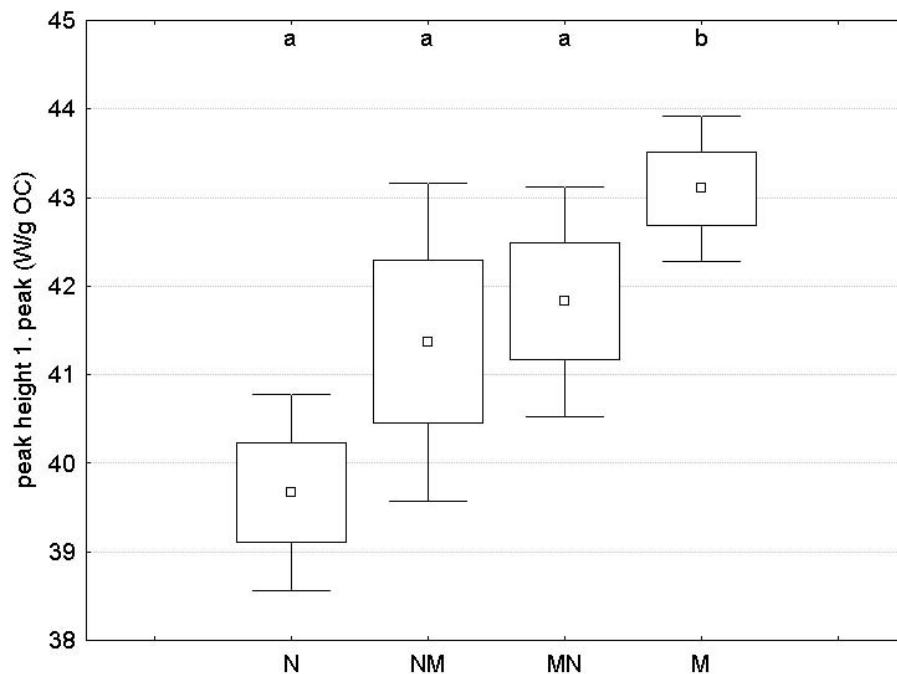


Fig. 2. Peak height of first exotherm for the four treatments. Box plots show mean, standard error SE, and $1.96 \times SE$. Different characters indicate significant differences for means ($P < 0.05$).

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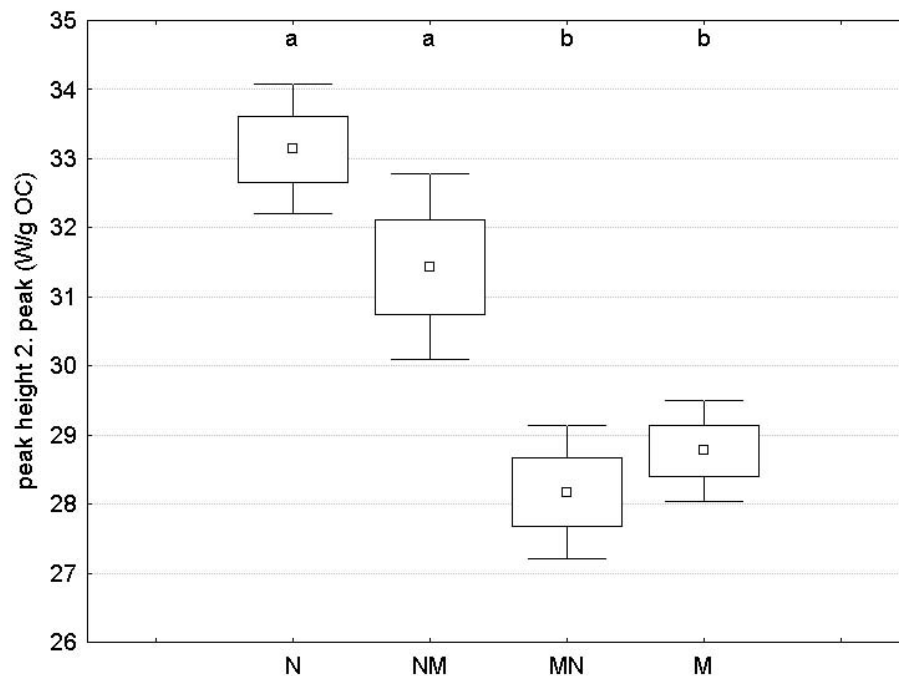


Fig. 3. Peak height of second exotherm for the four treatments. Box plots show mean, standard error SE, and $1.96 \times SE$. Different characters indicate significant differences for means ($P < 0.05$).

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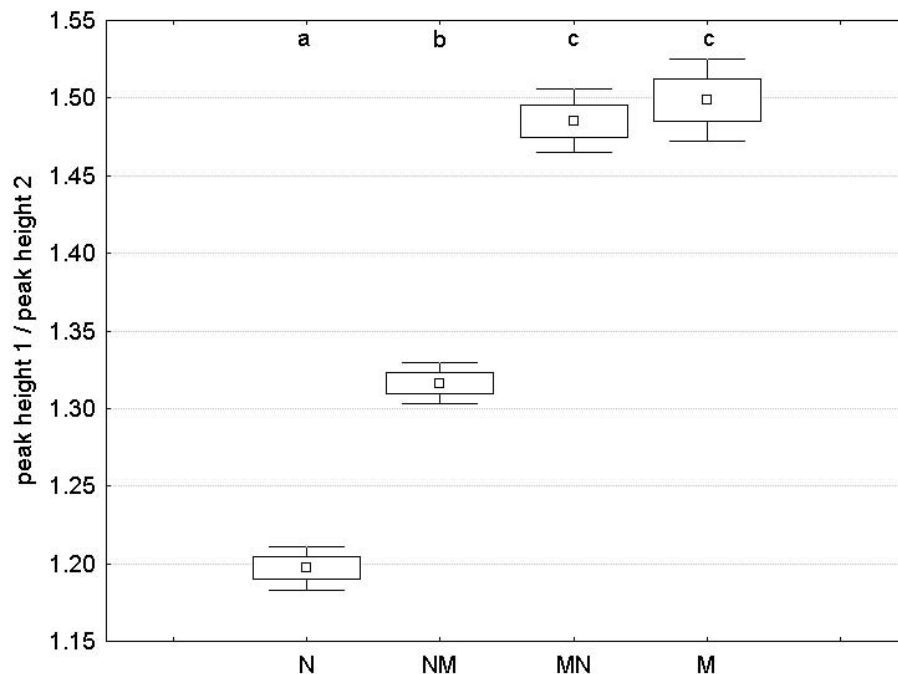


Fig. 4. Quotient of labile to stable SOM for the four treatments. Box plots show mean, standard error SE, and $1.96 \times SE$. Different characters indicate significant differences for means ($P < 0.05$).

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